DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 33

DETERMINATION OF CARBON IN STEEL AND IRON BY THE BARIUM CARBONATE TITRATION METHOD

BY

J. R. CAIN, Associate Chemist
Bureau of Standards

[JANUARY 31, 1914]

WASHINGTON
GOVERNMENT PRINTING OFFICE
1914

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS

1. The Effect of Preliminary Heat Treatment upon the Drying of Clays (53 pp.) *A. V. Bleininger*
2. The Strength of Reinforced Concrete Beams—Results of Tests of 333 Beams (first series) (200 pp.)........................*R. L. Humphrey and L. H. Losse*
3. Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, Together with Tests of Damp-Proofing and Waterproofing Compounds and Materials (127 pp.)......*R. J. Wig and P. H. Bates*
4. The Effect of Added Fatty and Other Oils upon the Carbonization of Mineral Lubricating Oils (14 pp.)..............................*C. E. Waters*
5. The Effect of High-Pressure Steam on the Crushing Strength of Portland Cement Mortar and Concrete (25 pp.)............................*R. J. Wig*
6. The Determination of Chromium, and Its Separation from Vanadium, in Steels (6 pp.)..*J. R. Cain*
7. The Testing of Clay Refractories, with Special Reference to Their Load-Carrying Capacity at Furnace Temperatures (78 pp.).................. *A. V. Bleininger and G. H. Brown*
8. A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on Its Quantitative Inclusion by the Phosphomolybdate Precipitate (20 pp.).......................................*J. R. Cain and J. C. Hostetter*
9. Density and Thermal Expansion of Linseed Oil and Turpentine (27 pp.) *H. W. Bearce*
10. Melting Points of Fire Bricks (17 pp.).............................*C. W. Kanolt*
11. Comparison of Five Methods Used to Measure Hardness (27 pp.)..*Ralph P. Devries*
12. Action of the Salts in Alkali Water and Sea Water on Cements (157 pp.) *P. H. Bates, A. J. Phillips, and R. J. Wig*
13. The Evaporation Test for Mineral Lubricating and Transformer Oils (13 pp.) *C. E. Waters*
14. Legal Specifications for Illuminating Gas (31 pp.)..*E. B. Rosa and R. S. McBride*
15. Surface Insulation of Pipes as a Means of Preventing Electrolysis (44 pp.).. *Burton McCollum and O. S. Peters*
16. Manufacture of Lime (130 pp.)..................................*W. E. Emley*
17. The Function of Time in the Vitrification of Clays (26 pp.).................... *G. H. Brown and G. A. Murray*
18. Electrolysis in Concrete (137 pp.)..*E. B. Rosa, Burton McCollum, and O. S. Peters*
19. Physical Testing of Cotton Yarns (31 pp.)........................*W. S. Lewis*
20. Determination of Sulphur in Illuminating Gas (46 pp.)................. *R. S. McBride and E. R. Weaver*
21. Dehydration of Clays (23 pp.)..............*G. H. Brown and E. T. Montgomery*
22. Effect of Overfiring Upon the Structure of Clays (23 pp.).................. *A. V. Bleininger and E. T. Montgomery*
23. Technical Control of the Collodial Matter of Clays (118 pp.)......*H. E. Ashley*
24. Determination of Phosphorus in Steels Containing Vanadium (11 pp.)..... *J. R. Cain and F. H. Tucker*
25. Electrolytic Corrosion of Iron in Soils (69 pp.)..*Burton McCollum and K. H. Logan*
26. Earth Resistance and Its Relation to Electrolysis of Underground Structures (— pp.)...................................*Burton McCollum and K. H. Logan*
27. Special Studies in Electrolysis Mitigation (55 pp.)...................... *E. B. Rosa and Burton McCollum*
28. Methods of Making Electrolysis Surveys (— pp.)...................... *Burton McCollum and G. H. Ahlbos*
29. Variations in Results of Sieving with Standard Cement Sieves (16 pp.) *R. J. Wig and J. C. Pearson*
30. Viscosity of Porcelain Bodies (9 pp.)..........*A. V. Bleininger and Paul Teetor*
31. Some Leadless Borosilicate Glazes Maturing at about 1,100° C (21 pp.) *E. T. Montgomery*
32. Electrolysis from Electric Railway Currents and Its Prevention: Experimental Test on a System of Insulated Negative Feeders in St. Louis (32 pp.)....................*E. B. Rosa, Burton McCollum, and K. H. Logan*
33. Determination of Carbon in Steels and Iron by the Barium Carbonate Titration Method...*J. R. Cain*

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 33

DETERMINATION OF CARBON IN STEEL AND IRON BY THE BARIUM CARBONATE TITRATION METHOD

BY

J. R. CAIN, Associate Chemist
Bureau of Standards

[JANUARY 31, 1914]

WASHINGTON
GOVERNMENT PRINTING OFFICE
1914

DETERMINATION OF CARBON IN STEEL AND IRON BY THE BARIUM CARBONATE TITRATION METHOD

By J. R. Cain

The disadvantages attending the use of weighed absorption tubes as means for accurately determining carbon dioxide obtained during the combustion of steels and irons are in part as follows:

1. The elaborate precautions required to prevent change of weight of the tube due to gain or loss of moisture, necessitating complications in the purifying train before and after the furnace and the use throughout the apparatus of drying agents of the same hygroscopic power.

2. Difficulties in weighing large glass vessels caused by electrical effects in wiping, by buoyancy, and by changes in temperature between balance room and laboratory.

3. The necessity for maintaining constant conditions with respect to the atmosphere within the tube, requiring sometimes a long period of aspiration after the combustion is completed.

4. The liability to error from access of gases containing sulphur and chlorine, which may be formed during combustion of the metal or of the carbonaceous residue therefrom.

5. The difficulty of determining whether the increase in weight of the tube is due solely to carbon dioxide.

6. The time lost in waiting for absorption tubes to reach a condition of equilibrium before weighing.

Those who have used absorption tubes for work requiring a high degree of accuracy know that neglect of one or more of the precautions indicated above may easily occasion errors ranging from several tenths of a milligram to 1 or more milligrams. It is evident, too, that if the complicated purifying train used with an absorption

tube gets out of order, or if the tube itself introduces error in some of the ways enumerated, it may often be a difficult matter to locate and correct the trouble. It is not surprising, therefore, that methods dispensing with the use of weighed potash bulbs, soda-lime tubes and the like are beginning to be used extensively by steel analysts. Of such methods the weighing of the carbon dioxide in the form of barium carbonate precipitate directly or after conversion into sulphate have been much used, the sulphate method abroad,[1] and the carbonate method in this country. Thus, of 62 prominent American laboratories (representing manufacturers, consumers, and testing laboratories) 32 used the potash bulb, 24 weighed the carbon as barium carbonate, 3 titrated the excess of barium hydroxide, 2 used soda-lime tubes, and 1 weighed an absorption tube filled with barium hydroxide.[2]

It is evident, in estimating the carbon dioxide by weighing the barium carbonate precipitate, or the sulphate obtained from it, that the difficulties mentioned above as peculiar to weighed absorption tubes, except No. 4, are eliminated or minimized; access of sulphur trioxide would still tend to cause high results.[3] If, however, the barium carbonate is measured by filtering it off and titrating it against standard acid, due regard being had to proper conditions for filtration and washing, there is no likelihood of error from any of the causes enumerated. The principle of this method is described in most standard textbooks on quantitative and volumetric analysis, but there seems to have been but little application in steel analysis.

The purpose of this paper is to show the special suitability of this procedure for accurate and fairly rapid steel analysis, taking up in order the sources of error or difficulty and the means of avoiding or minimizing these, and finally giving the results obtained by a series of analyses of pure sugar and of Bureau of Standards analyzed irons and steels. Without further consideration it can be seen that the adoption of this method at once simplifies the purifying train

[1] Bauer and Deiss: Probenahme und Analyse von Eisen und Stahl, 1912, p. 121.

[2] Data communicated to the author as member of a technical committee on steel analysis.

[3] There is but little likelihood of SO_3 being produced in burning steel and iron. Any small amounts of $BaSO_3$ resulting thereby would be removed by washing (see sec. 1 on Filtration and washing), the solubility of $BaSO_3$ being approximately .002 gram per 100 cc of water at 20° (Seidell "Solubilities of Inorganic and Organic Substances," 1907).

required after the furnace. Nothing at all likely to be present in the escaping gases can affect the results if we except finely divided oxides carried over mechanically as the result of a very violent combustion. No such oxides were noticed during this work or during the analyses of many other samples by different methods. If there is any reason to suspect their presence, a simple filter made by filling a U-tube with 20-mesh quartz, previously carefully washed with hydrochloric acid and water, will remove them.

The points involving sources of error which were investigated were (1) completeness of absorption of the carbon dioxide, (2) amount of washing necessary to remove the excess of barium hydroxide, (3) solubility of barium carbonate in the wash water, and (4) exclusion of extraneous alkaline substances. In addition there was devised means for the rapid filtration and washing of the barium carbonate with exclusion of carbon dioxide from the air.

I. COMPLETENESS OF ABSORPTION

This was established by burning sugar in amounts giving approximately the weights of carbon dioxide obtained during steel analysis, comparing the percentages of carbon obtained with the theoretical. As a further check two eight-bulb Meyer tubes (shown in half size in Fig. 1) were worked in series. So long as a moderate rate of bubbling was maintained no cloudiness was ever observed in the second tube. In this connection McCoy and Tashiro[4] have shown that 1.0×10^{-7} g of CO_2 can be recognized as a turbidity. If, however, the oxygen is passed too rapidly, particularly when burning steels containing more than 1 per cent carbon, some CO_2 may reach the second tube. The proper rate of gas current to retain all the CO_2 in the first tube is easily established by the operator after a few trials.

II. AMOUNT OF WASHING NECESSARY

Barium carbonate itself reacts alkaline to phenolphthalein, consequently this indicator can not be used to show when all of the barium hydroxide has been removed. The practical question as to how much washing was necessary was decided by washing the

[4] Original communication, 8th Int. Congr. Appl. Chem., 1, p. 361, 1912.

barium carbonate obtained from the combustion of accurately weighed amounts of sugar until results agreeing with the theoretical, within a small experimental limit, were obtained. The amount of wash water thus determined was increased by 25 per cent. About 150 cc wash water was usually found sufficient. The results are summarized in the recommendations later, under the head "Filtration and washing of the barium carbonate."

III. SOLUBILITY OF BARIUM CARBONATE IN WASH WATER

The possible effect of the slight hydrolysis of the barium carbonate in causing low results by solvent action of the wash water was studied by comparing the results obtained when determining the barium carbonate from the combustion of the same weights of sugar, first by washing as above described, and then with twice and three times the amount of water recommended. The results showed that the error from hydrolysis is negligible for present purposes. (See table and footnotes 8 and 9, p. 11.) Holleman[5] found the solubility of freshly precipitated $BaCO_3$ in CO_2-free water to be 1 part $BaCO_3$ in 64 070 parts water at 8.8° and 1 part in 45 566 parts water at 24.2°, or approximately 1 part in 50 000 at the temperature of the laboratory during this work, i. e., 20° to 22°. On this basis 150 cc wash water (see preceding section) would dissolve about 0.0003 g $BaCO_3$ = 0.000018 g carbon. This would be negligible for present purposes, and the amount dissolved would be really less than this because of the repression of solubility during the first washings by the barium hydroxide still present; also it is quite possible that in the rapid passage through the filter there has not been sufficient time for the wash water to become saturated with barium carbonate. Holleman's results are in good agreement with those of Bineau.[6] Holleman called attention to the fact, also recorded by Bineau, that the presence of carbon dioxide in water appreciably raises the solubility of barium carbonate, and Holleman explains in this way the solubility of 1 part in 14 137 parts of water observed by Fresenius, who left the carbonate in contact with water exposed to the air for several days.

---

[5] Zs. physik. Chem., 12, p. 135, 1893.

[6] Ann. chim. phys. (3), 51, p. 290.

IV. POSSIBLE SOURCES OF EXTRANEOUS ALKALINE SUBSTANCES

These are (1) substances derived by action of water on the bottles containing the CO_2-free water mentioned later; such action should be avoided by choosing a good quality of glass bottle; Jena glass containers were found satisfactory; (2) alkali carried over mechanically from soda lime guard tubes by the air used to force out CO_2-free water; thick plugs of glass wool will remove this source of danger; (3) action of barium hydroxide on the walls of the Meyer tubes; these tubes should not give up alkaline substances to the standard acid after barium hydroxide has stood in them for one-half hour and the tubes have then been thoroughly washed with alkali-free water; (4) action of barium hydroxide on filtering material; glass wool as a filling material is absolutely excluded on this ground; quartz has been found very satisfactory (see description of filtering apparatus); amphibole asbestos for the felt was found suitable from this standpoint as well as because of its resistance to attack by N/10 hydrochloric acid.

V. FILTRATION AND WASHING OF THE BARIUM CARBONATE

This is carried out with the apparatus shown in Fig. 1. The cut is approximately half-size and is self-explanatory. S is a two-way stopcock connected to the suction pipe. The rubber tubing connected to the Meyer tube should be of best grade black rubber, and the lengths used should be chosen so as to permit of easy manipulation of the tube. The Meyer tube is connected or disconnected by the rubber stoppers which are left always attached to the rubber tubes. The carbon filter C is fitted with a perforated porcelain plate, sliding easily.

The funnel is prepared for filtrations by making a felt of asbestos on the porcelain disk, using asbestos which has been digested for several hours with strong hydrochloric acid and then washed free of acid. On top of the asbestos is placed a layer of similarly washed quartz of the height shown in the figure. A mixture of grains of various sizes (approximately 50 per cent passing a 20-

mesh and the remainder passing a 10-mesh and remaining on a 20-mesh sieve) is suitable. A mixture of quartz and asbestos works well and may be simply obtained by filling the funnel with a suspension of asbestos and delivering the quartz to the funnel from a beaker by means of a strong jet of water from the wash bottle, while maintaining a gentle suction. In this way the asbestos is properly mixed with the quartz. Proper attention to these details will be found to greatly expedite filtration. The stopper is now inserted in the funnel, the Meyer tube connected as shown, and the liquid and precipitate sucked into the funnel.

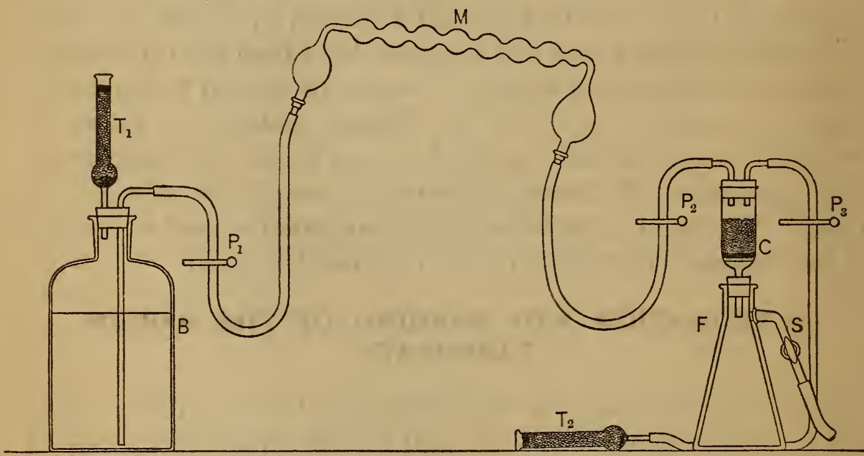

Fig. 1.—*Apparatus for filtering and washing barium carbonate*

Only very gentle suction should be used. When necessary P3 is opened to admit air back of the column of liquid in the Meyer tube.

When the contents of the tube have all been transferred the large bulb nearest B is about half filled with water by opening P1; the stopcock S is operated during this and subsequent operations so as to maintain a gentle suction. M is now manipulated so as to bring the wash water in contact with all parts of the interior, after which the water is sucked out through C; P2 is left open during this and subsequent washings. After eight washings, as directed, allowing the wash water to drain off thoroughly each time before adding more, M may be detached, the stopper removed

from the funnel, and the washing completed by filling C to the top with CO_2-free water, sucking off completely and repeating the operation once. Air is now admitted through the side opening of S; C is removed and the porcelain disk carrying the quartz, asbestos, and barium carbonate is shoved, by means of a long glass rod, into the flask used for titrations, removing from the sides of C any adhering particles by a jet of water from the wash bottle.

VI. APPARATUS AND SOLUTIONS USED

1. APPARATUS

The method requires no modification of any of the accepted appliances for the combustion of iron and steel. In the present work both gas and electrically heated furnaces were used. As already stated, there was no purifying train after the furnace, the Meyer tube being directly attached. Before the furnace was an electrically heated porcelain tube filled with copper oxide, followed by a calcium chloride tower filled with stick potassium hydroxide. Steels and irons were burned on a bed of alkali and carbon free alundum contained in a platinum boat. The blanks obtained by carrying through a complete determination, including filtration, washing, etc., but with omission of any carbon-containing substance, were usually 0.0 cc and never more than 0.05 cc of N/10 hydrochloric acid, showing not only that the oxygen was sufficiently purified and the apparatus in good condition, but that the operations of filtration, washing, etc., introduced no appreciable positive error.

2. SOLUTIONS

Tenth-Normal Hydrochloric Acid.—Standardized by any of the accepted methods, or as follows: 20 cc of the approximately N/10 acid is measured out with a pipette, 5 cc of nitric acid (1 to 1 by volume) is added, and the silver chloride precipitated by an excess of silver nitrate solution in a volume of 50 to 60 cc. After digesting at 70° to 80° until the supernatant liquid is clear, the chloride is filtered off on a tared Gooch filter and washed with water con-

taining 2 cc of nitric acid per 100 cc of water until freed from silver. After drying to constant weight at 130°, the increase of weight over the original tare is noted and the strength of the hydrochloric acid calculated on the basis of the weight of silver chloride thus obtained, afterwards adjusting to the strength prescribed. Several concordant determinations with varying amounts of acid should be made. One cc N/10 HCl = 0.0006 g carbon.

Tenth-Normal Sodium Hydroxide Solution.—Standardized against the hydrochloric acid solution, with methyl orange as indicator. This solution is conveniently stored in a large glass bottle fitted with a soda-lime guard tube and arranged for delivering the solution by air pressure.

Methyl Orange.—0.02 g dissolved in 100 cc of hot water and filtered.

Barium Hydroxide Solution.—A saturated solution filtered and stored in a large reservoir from which it is delivered by air pressure, protecting from carbon dioxide by a soda-lime tube. Three or four small bulbs of the Meyer tube are filled, and CO_2-free water is added until the remaining small bulbs are filled. When burning products high in carbon the stock solution may be used undiluted.

Carbon Dioxide-Free Water.—This is conveniently made by passing air for a sufficient length of time through a soda-lime tube and into a 6 or 8 liter bottle filled with pure distilled water. The water is delivered by CO_2-free air under pressure.

VII. THE METHOD.

The combustion is carried out in the usual manner, care being taken not to pass the oxygen too rapidly. After filtering, washing, and transferring the contents of the filter to a flask, as described under "Filtration and washing of the barium carbonate," a slight excess of the standard acid is added from a burette, using a portion to rinse out the Meyer tube, and the excess of acid is then titrated against the sodium hydroxide, using methyl orange as indicator.

Results Obtained by Barium Carbonate Titration Method

Material	Weight	Carbon present	Carbon found	Difference
	g	g	g	g
Sugar [7]	0.0100	0.00421	[8] 0.00427	+0.00006
	.0100	.00421	.00420	− .00001
	.0100	.00421	.00430	+ .00010
	.0200	.00842	.00840	− .00002
	.0200	.00842	.00860	+ .00018
	.0200	.00842	.00860	+ .00018
	.0300	.01263	.01280	+ .00017
	.0300	.01263	.01280	+ .00017
	.0300	.01263	[9] .01275	+ .00012
Bessemer steel, B. S. No. 23	1.000	[10] .00805	.00805	.0000
	1.000	.00805	.00805	.0000
	1.000	.00805	.00805	.0000
	1.000	.00805	[8] .00800	− .00005
Bessemer steel, B. S. No. 10b	1.000	[10] .00373	.00372	− .00001
	1.000	.00373	.00372	− .00001
Pig iron C, B. S. No. 5b	1.000	[10] .02726	.02710	− .00016
	1.000	.02726	.02710	− .00016

Mean error, sugar .... +0.000094
Mean error, steels and iron .... − .000056

[7] B. S. Standard sample No. 17. A 1 per cent aqueous solution was made and the required amounts were delivered into a porcelain boat from a burette. After careful evaporation of the water the sample was burned.

[8] Washed with double the usual amount of wash water. The second portion of wash water was titrated against the N/10 hydrochloric acid; the amounts used after deducting the blank when titrating the same quantity of the water used for washing were 0.10 cc and 0.15 cc.

[9] Washed with three times the usual amount of wash water.

[10] Certificate values.

The results given in the table show that the method is as accurate as the weighing methods. It is not so subject to disturbing influences and requires less elaborate apparatus than those methods do.

VIII. NOTES AND PRECAUTIONS

1. After a little practice a precipitate can be filtered and prepared for titration in five minutes.

2. When working with steels high in carbon (above 1 per cent) it is advisable not to use more than 1 g, in order that filtration may be sufficiently rapid.

3. For very accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished the Meyer tube should be completely filled with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

4. The flask containing the carbonate should be very thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

5. The rubber tube connecting B (see Fig. 1) to the Meyer tube should be washed with a little water from B before beginning determinations each day.

I am indebted to Mr. H. L. Cleaves, of this Bureau, who prepared the drawing of the filtering apparatus and made many determinations on steels which will appear in a later publication.

WASHINGTON, January 31, 1914.

ADDITIONAL COPIES
OF THIS PUBLICATION MAY BE PROCURED FROM
THE SUPERINTENDENT OF DOCUMENTS
GOVERNMENT PR NTING OFFICE
WASHINGTON, D. C.
AT
5 CENTS PER COPY
▽